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A First-Order Phase Transition between Crystal Phases in the Shift Model

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We describe rigorously a many-body model of interacting classical particles exhibiting the following behavior at zero temperature: as the pressure varies through a critical value, the system goes through a first-order phase transition between different crystal phases. Moreover, at the critical pressure the system is demonstrably a mixture of the two phases.

KEY WORDS: Phase transition; crystal; ground state.

1. INTRODUCTION

It remains at heart obscure why all forms of matter tend to be crystalline rather than amorphous at low temperature. After all, a crystalline configuration is rarely if ever observed(1) for *small* clusters of molecules (less than 100, say); it must be a question of extending patterns to *large* clusters that forces the crystalline symmetry. This is one of the major unsolved problems of condensed matter physics.(2)

Most of the effort on this problem (see Ref. 3 and references therein) has centered on the molecular-bonded solids, using classical mechanics and Lennard–Jones-type forces. Since even the various close-packed crystals yield extremely close molar energies, it has been necessary to concentrate on models in one and two dimensions; since Mermin's theorem(4) indicates a lack of long range order for temperature $T > 0$ in these dimensions, one is lead to investigate the case $T = 0$.

Below we describe rigorously a many-body model of interacting classical particles exhibiting the following behavior at low (zero) temperature: as

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the pressure varies through a critical value, the system goes through a first-order phase transition between different crystal phases. Moreover, at the critical pressure the system is demonstrably a mixture of the two phases. (For a general reference see Ref. 2.)

Our model (which we call the shift model) is one dimensional with interaction potential:

$$\Phi(r) = \begin{cases} +\infty, & 0 \leqslant r < 0.96 \\ -100r + 97.8, & 0.96 \leqslant r \leqslant 0.98 \\ -r + 0.78, & 0.98 \leqslant r \leqslant 2 \\ 1.16 - 3.54, & 2 \leqslant r \leqslant 3 \\ 0.1r - 0.36, & 3 \leqslant r \leqslant 3.6 \\ 0, & 3.6 \leqslant r \end{cases}$$

Note that the range of Φ is less than 4(0.96) so each particle interacts with at most three particles on each side of it on the line. (The graph of Φ is continuous for $r > 0.96$, and composed of line segments.)

Throughout this paper we assume a fixed number $N \geqslant 11$ of particles in the system. The total (potential) energy $E^T(x)$ of a configuration (i.e., set of particle positions) $x = \{x_1, x_2, \ldots, x_N\}$, $x_{k+1} > x_k$, depends only on the "spacing sequence" $\{x_2 - x_1, x_3 - x_2, \ldots, x_N - x_{N-1}\}$ and can be decomposed:

$$E^T(x) = (1/4) \sum_{j=1}^{N-4} E_j(x) + C(x)$$

where

$$\begin{aligned} E_j(x) = \big[&\Phi(x_{j+1} - x_j) \\ &+ \Phi(x_{j+2} - x_{j+1}) + \Phi(x_{j+3} - x_{j+2}) + \Phi(x_{j+4} - x_{j+3})\big] \\ &+ (4/3)\big[\Phi(x_{j+2} - x_j) + \Phi(x_{j+3} - x_{j+1}) + \Phi(x_{j+4} - x_{j+2})\big] \\ &+ 2\big[\Phi(x_{j+3} - x_j) + \Phi(x_{j+4} - x_{j+1})\big] \end{aligned}$$

and $C(x)$ (due to undercounting the nine interactions involving the three particles at each end) is bounded as $N \to \infty$. (When considering one E_j we also denote $\{x_j, x_{j+1}, x_{j+2}, x_{j+3}, x_{j+4}\}$ by x.) Note that $C(x) \equiv 0$ if periodic boundary conditions are used.

We are concerned with low-temperature behavior. The statistical ensemble (the "pressure ensemble"[(2)]) corresponding to fixed pressure p and inverse temperature β has density $\exp\{-\beta[E^T(x) + pV^T]\}$, where V^T is the (variable) volume: $V^T \geqslant x_N - x_1$. Therefore at zero temperature the ensemble (i.e., probability measure) is concentrated on those configurations x which minimize $E^T(x) + pV^T$, where now $V^T = V^T(x) = x_N - x_1$. Our main task is thus to minimize $E^T(x)$ (with variable volume constraint). It is noteworthy that we can accurately approximate such a minimizing configuration by instead minimizing each $E_j(x)$ and noting that the N-particle configurations which do this can be chosen to be "compatible" in the sense that they minimize $E_j(x)$ for all j simultaneously. We minimize each $E_j(x)$ with x subject to the variable constraint of given volume $V_j(x) \equiv x_{j+4} - x_j$.

2. ESTIMATES

First we note from simple considerations that to minimize $E_j(x) + pV_j(x)$, $p \geqslant 0$ fixed, we need only consider x such that $3.84 \leqslant V_j(x) \leqslant 4$. It is convenient to reparametrize volume by $w = 4 - V_j$, $0 \leqslant w \leqslant 0.16$. Define

$$\tilde{E}(w) = \min\left[E_j(x) \mid x_{j+4} - x_j = 4 - w\right]$$

$$F(p) = \min\left[\tilde{E}(w) + p(4 - w) \mid 0 \leqslant w \leqslant 0.16\right]$$

and let $E_{\text{eq}}(w)$ be the value of $E_j(x)$ when the x_k are equally spaced, $x_{k+1} - x_k = 1 - w/4$. In computing $\tilde{E}(w)$ we will consider separately the intervals $0 \leqslant w \leqslant 0.08$ and $0.08 \leqslant w \leqslant 0.16$, and we begin with the former.

It is easy to check that for $0 \leqslant w \leqslant 0.08$, $E_{\text{eq}}(w) = E_{\text{eq}}(0) - 0.48w$. To compute $\tilde{E}(w)$ we consider a configuration of five equally spaced particles with $x_{j+4} - x_j = 4 - w$ and compute the change in energy under arbitrary displacement of x_{j+1}, x_{j+2}, x_{j+3}. Let $E_{a,b,c}$ denote the value of $E_j(x)$ when x_{j+1} (resp. x_{j+2}, x_{j+3}) is increased by the amount a (resp. c, b) from its equal-spacing position; a, b, c are possibly negative. It is easy to see from force considerations that in any minimum configuration ($0 \leqslant w \leqslant 0.08$) no two particles are closer than 0.98 and also that $|c| \leqslant w/2$. There are three basic cases to consider: $a \geqslant b \geqslant 0$, $b \geqslant a \geqslant 0$ and $a \geqslant 0 \geqslant b$. (The case $a \leqslant 0 \leqslant b$ cannot lead to a minimum unless $a = b = 0$.) Assuming $a \geqslant b \geqslant 0$ one can show that the following inequalities are sharp: For $0 \leqslant w \leqslant 0.22/85$, $E_{a,b,c} \geqslant E^{(1)}(w) \equiv E_{\text{eq}}(w) + 1.06(w - 0.04) + 1.7w/3$ (with equality when $w = 0$ only if $a = b = 0.02$, $c = 0$), and for $0.22/85 \leqslant w \leqslant 0.08$, $E_{a,b,c} \geqslant E^{(2)}(w) \equiv E_{\text{eq}}(w) + 2.96(w/2 - 0.04)/3$ (with equality when $w = 0.08$ only if $a = b = c = 0$).

Assuming $b \geqslant a \geqslant 0$, one can show that the following inequalities are sharp: For $0 \leqslant w \leqslant 0.02$, $E_{a,b,c} \geqslant E^{(3)}(w) \equiv E_{\text{eq}}(w) + 1.06(2w - 0.04)$ (with equality when $w = 0$ only if $a = b = 0.02$, $c = 0$), and for $0.02 \leqslant w \leqslant 0.08$, $E_{a,b,c} \geqslant E_{\text{eq}}(w)$ (with equality when $w = 0.08$ only if $a = b = c = 0$).

Finally, assuming $a \geqslant 0 \geqslant b$ one can show that the following inequality is sharp: $E_{a,b,c} \geqslant E^{(2)}(w)$ (with equality when $w = 0.08$ only if $a = b = c = 0$.) Note that $E^{(3)}(w) > E^{(1)}(w)$ for $0 < w \leqslant 0.08$, $E^{(2)}(w) > E^{(1)}(w)$ for $0 \leqslant w < 0.22/85$ and $E^{(2)}(w) < E^{(1)}(w)$ for $0.22/85 < w \leqslant 0.08$. Thus $\tilde{E} = E^{(1)}$ on $[0, 0.22/85]$ and $\tilde{E} = E^{(2)}$ on $[0.22/85, 0.08]$.

Next we compute $\tilde{E}(w)$ for $0.08 \leqslant w \leqslant 0.16$. It is easy to check that $E_{\text{eq}}(w) = E_{\text{eq}}(3.92) + 98.52(w - 0.08)$. Using the obvious constraint $0.96 \leqslant x_{k+1} - x_k \leqslant 0.98$ we find the sharp inequalities: For $0.08 \leqslant w \leqslant 0.12$, $E_{a,b,c} \geqslant E^{(4)}(w) \equiv E_{\text{eq}}(w) - 1.48(w - 0.08)/3$ (with equality when $w = 0.08$ only if $a = b = c = 0$) and for $0.12 \leqslant w \leqslant 0.16$, $E_{a,b,c} \geqslant E^{(5)}(w) \equiv E_{\text{eq}}(w) - 1.48(0.16 - w)/3$ (with equality when $w = 0.16$ only if $a = b = c = 0$.) Therefore $\tilde{E} = E^{(4)}$ on $[0.08, 0.12]$ and $\tilde{E} = E^{(5)}$ on $[0.12, 0.16]$.

Now consider $F(p)$, using the facts

$$\frac{d}{dw} E^{(1)}(w) = 4.34/3$$

$$\frac{d}{dw} E^{(2)}(w) = 0.04/3$$

$$\frac{d}{dw} E^{(4)}(w) = 294.08/3$$

$$\frac{d}{dw} E^{(5)}(w) = 297.04/3$$

For $p = 0$ it is clear that $F(0) = \tilde{E}(0)$, and $E_j(x) = F(0)$ only for the spacing sequences

$$\{0.98, 1.02, 0.98, 1.02\} \text{ or } \{1.02, 0.98, 1.02, 0.98\} \tag{1}$$

To determine $F(p)$ for $p > 0$ we first use the fact that as a function of w, $\tilde{E}$ is concave downward on $[0, 0.08]$. This is the feature of our model producing the discontinuous decrease of volume with increasing pressure since it follows that there is a critical value p_c of p (easily seen to be $p_c = 0.05$) such that for $0 \leqslant p < p_c$, $F(p) = \tilde{E}(0) + 4p$ with $F(p) = E_j(x) + pV_j(x)$ only for $V_j(x) = 4$ and either of the "shifted" spacing sequences in (1), while for $p_c < p < 297.04/3$, $F(p) = E_j(x) + pV_j(x)$ only for $V_j(x) = 3.92$ and equal spacing, of size 0.98.

For each p, $0 \leqslant p < 297.04/3$, $p \neq p_c$, define

$$V(p) = \begin{cases} 4, & 0 \leqslant p < p_c \\ 3.92, & p_c < p < 297.04/3 \end{cases}$$

Next note that crude estimates show that if $V_j(x) = 4 + w$, $0 \leqslant w \leqslant 1$, then $E_j(x) \geqslant E_{\text{eq}}(w) - 0.0424 + 1.64w/3$. Combining this with our results on $\tilde{E}(w)$, we see that for small w of either sign: if $V_j(x) = 4 + w$, $E_j(x) - \tilde{E}(0) \geqslant 1.64|w|/3$, and if $V_j(x) = 3.92 + w$, $E_j(x) - \tilde{E}(0.08) \geqslant 0.04|w|/3$.

3. CONCLUSION

Thus from the calculations above we immediately conclude that there exist finite constants C_k independent of N such that if for a system of N

particles $x = x(N)$ minimizes $E^T(x) + pV^T(x)$: (a) $|E^T(x(N)) - (N/4)\tilde{E}(4 - V(p))| < C_1$; (b) $|V^T(x(N)) - NV(p)/4| < C_2$; (c) for large N, $x(N)$ "looks like" the appropriate crystal for that pressure, i.e., given $\epsilon > 0$, at most $C_3/\epsilon N$ blocks of five consecutive particles can differ from the appropriate perfect crystal block by more than ϵ (measured with the Euclidean norm in $\mathbb{R}^5$.)

We thus have the existence and value of the asymptotic energy per particle and volume per particle:

$$e(p) = \lim_{N\to\infty} E^T(x(N))/N = (1/4)\tilde{E}(4 - V(p))$$

$$= \begin{cases} E_{\text{eq}}(0)/4 - 0.0106, & 0 \leqslant p < p_c \\ E_{\text{eq}}(0)/4 - 0.0096, & p_c < p < 297.04/3 \end{cases}$$

$$v(p) = \lim_{N\to\infty} V^T(x(N))/N = V(p)/4$$

$$= \begin{cases} 1, & 0 \leqslant p < p_c \\ 0.98, & p_c < p < 297.04/3 \end{cases}$$

At $p = p_c$ the volume is no longer constrained. It follows immediately from our calculations of $\tilde{E}$ that there exists a finite constant C_4 independent of N such that if $x(N)$ is a configuration minimizing $E^T(x) + p_c V^T(x)$, and $v = V^T(x(N))/N = aV(p_c - 0) + (1 - a)V(p_c + 0)$ for some a in $[0, 1]$, then: (d) For large N, $x(N)$ "looks like" a mixture of the two crystal phases, i.e., given $\epsilon > 0$ at most $C_4/\epsilon N$ blocks of five consecutive particles differ from one or the other perfect crystal block by at most ϵ. This implies that $x(N)$ consists of a small number of long chains of essentially perfect crystals of the two types, and, to obtain the proper volume, the number of blocks B_L of the low-pressure phase and B_H of the high-pressure phase must be in the proportion: $B_L/B_H = a/(1 - a)$.

Finally we note that simple force estimates show that sufficiently small changes in the interaction potential, including smoothing its corners, would preserve the first-order transition while making the volume a strictly decreasing function of $p \neq p_c$; we expect they would also preserve the crystal phase structure, though this seems harder to prove.

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